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Communications

Isolation and Structural Characterization of a Polyhydrido Lanthanide Cluster Complex Consisting of "$(C_5Me_4SiMe_3)LuH_2$" Units

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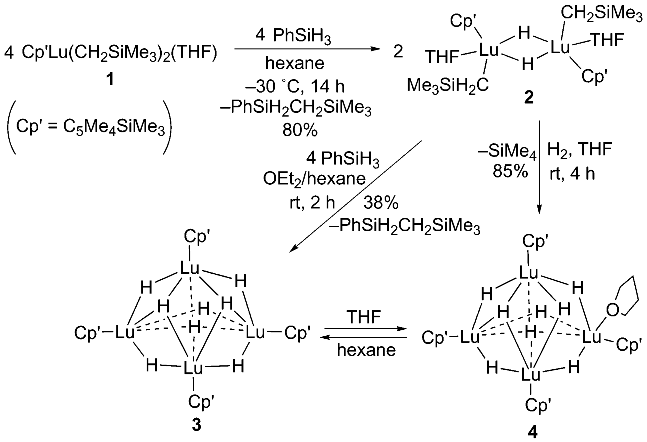
Summary: Reaction of the mixed alkyl/hydride complex $[Cp'Lu(CH_2SiMe_3)(\mu\text{-}H)(THF)]_2$ (**2**; $Cp' = C_5Me_4SiMe_3$) *with 1 equiv of* $PhSiH_3$ *(per Lu) in benzene or* OEt_2 *afforded the polyhydrido cluster* $[Cp'LuH_2]_4$ (**3**), *while hydrogenolysis of* **2** *with* H_2 *(1 atm) in THF yielded the THF-coordinated complex* $[Cp'Lu(\mu\text{-}H)_2]_4(THF)$ (**4**). *Complexes* **3** *and* **4** *are interconvertible, without decomposition or ligand redistribution.*

Organolanthanide hydride complexes have occupied an especially important place in the development of organolanthanide chemistry, because of their novel activity in various catalytic processes.[1] However, despite the importance of such species, these compounds have so far been limited almost to monohydrido complexes with two ancillary ligands such as metallocene hydrides. Although dihydrido lanthanide complexes with one ancillary ligand are anticipated to show more flexible reactivities, such compounds have hardly been explored because of ligand scrambling problems.[2] The isolation and structural characterization of a salt-free dihydrido lanthanide complex of the type "LMH_2" remained a challenge.

Scheme 1



An early attempt to synthesize a mono(cyclopentadienyl)lutetium dihydride complex through hydrogen-

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[1] For recent reviews, see: (a) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161. (b) Marques, N.; Sella, A.; Takats, J. *Chem. Rev.* **2002**, *102*, 2137. (c) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1. (d) Hou, Z.; Wakatsuki, Y. In *Science of Synthesis*; Imamoto, T., Noyori, R., Eds.; Thieme: Stuttgart, Germany, 2002; Vol. 2, p 849. (e) Ephritikhine, M. *Chem. Rev.* **1997**, *97*, 2193. (f) Yasuda, H. *Top. Organomet. Chem.* **1999**, *2*, 255. (g) Anwander, R. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Hermann, W. A., Eds.; VCH: Weinheim, Germany, 1996; p 866. (h) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (i) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Lappert, M. F., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 4, p 11. (j) Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.

[2] Reviews on mono(cyclopentadienyl)-supported lanthanide complexes: (a) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953. (b) Hou, Z.; Wakatsuki, Y. *J. Organomet. Chem.* **2002**, *647*, 61.

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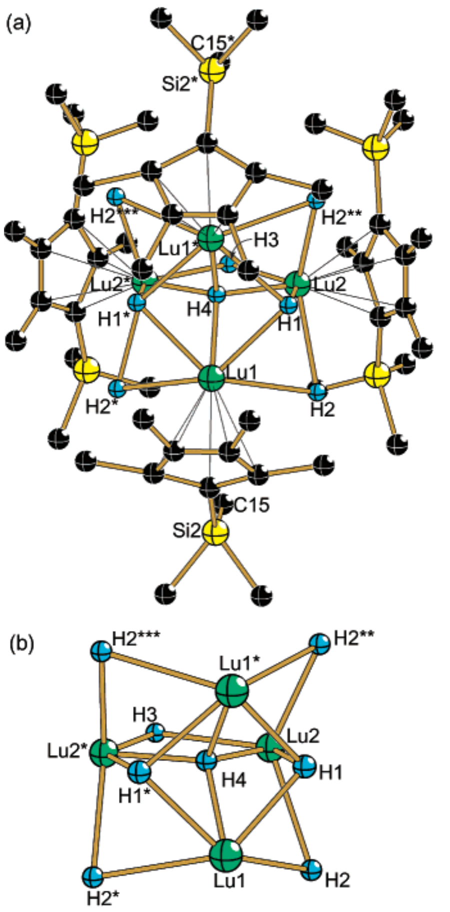

Figure 1. (a) X-ray structure of **3**. The $C_5Me_4SiMe_3$ groups on Lu2 and Lu2* are disordered. (b) Structure of the Lu_4H_8 core in **3**. Selected bond distances (Å): Lu1−H1, 2.45(6); Lu2−H1, 1.98(8); Lu1−H2, 2.70(5); Lu2−H2, 2.54(5); Lu2−H3, 2.51(7); Lu1−H4, 2.11(7); Lu2−H4, 2.03(5); Lu1−Cp′(av), 2.62(1); Lu2−Cp′(av), 2.50(1).

olysis of $(C_5Me_5)Lu(CH_2SiMe_3)\{CH(SiMe_3)_2\}(THF)$ or $(C_5Me_5)Lu(CH_2CMe_3)_2(THF)$ did not afford an isolable hydride species.[3] Similar hydrogenolysis of the yttrium bis(alkyl) complex $(C_5Me_4SiMe_2X)Y(CH_2SiMe_3)_2(THF)$ was recently reported to yield a pentane-soluble complex with the probable formula $[(C_5Me_4SiMe_2X)YH_2]_4{\cdot}2THF$ (X = Me, Ph), but the structures of these species remained unidentified.[4] The only structurally characterized dihydrido lanthanide species reported so far in the literature was obtained in the heteropolymetallic form $[(C_5Me_5)Sm(\mu\text{-}H)_2]_6[(\mu\text{-}H)K(THF)_2]_3$ by combination with the "$KH(THF)_2$" unit.[5] To our knowledge, a well-defined salt-free dihydrido lanthanide complex has not been previously reported. We report here the first example of a structurally characterized salt-free dihydrido lanthanide complex, $[Cp'Lu(\mu\text{-}H)_2]_4(THF)_n$ ($n = 0, 1$, $Cp' = C_5Me_4SiMe_3$), which adopts a tetrameric form through μ-H bridges.[6−8] This complex could be easily obtained by hydrogenolysis of a novel mixed alkyl/hydride lutetium complex, $[Cp'Lu(CH_2SiMe_3)(\mu\text{-}H)(THF)]_2$.

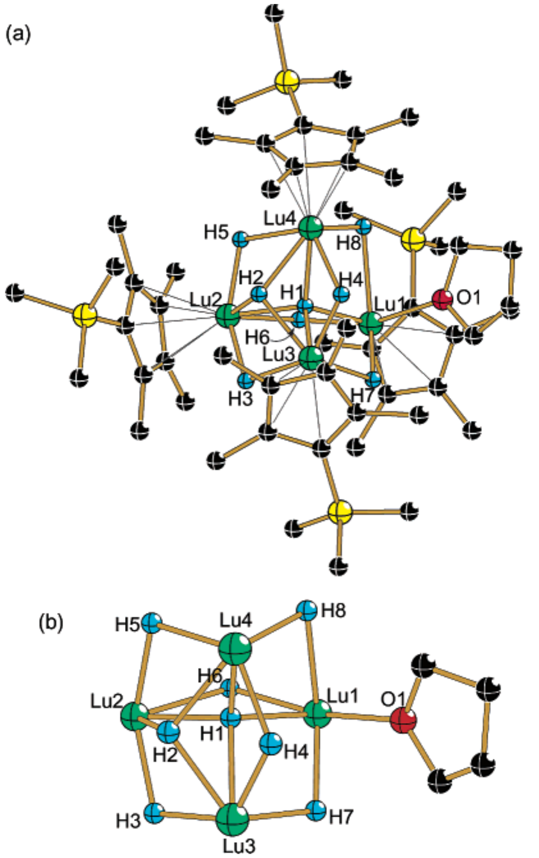

Figure 2. (a) X-ray structure of **4**. (b) Structure of the $Lu_4H_8(THF)$ core in **4**. Selected bond distances (Å): Lu1−H1, 2.11(5); Lu2−H1, 1.95(6); Lu3−H1, 2.33(5); Lu4−H1, 2.14(6); Lu2−H2, 2.09(6); Lu3−H2, 2.02(5); Lu4−H2, 2.06(6); Lu2−H3, 1.92(5); Lu3−H3, 2.26(6); Lu3−H4, 1.99(2); Lu4−H4, 1.85(3); Lu2−H5, 1.98(6); Lu4−H5, 2.44(6); Lu1−H6, 1.94(6); Lu2−H6, 2.49(5); Lu1−H7, 2.01(5); Lu3−H7, 2.42(5); Lu1−H8, 2.41(6); Lu4−H8, 2.26(5); Lu1−Cp′(av), 2.591(5); Lu2−Cp′(av), 2.568(6); Lu3−Cp′(av), 2.585(6); Lu4−Cp′(av), 2.578(6); Lu1−O1, 2.373(4).

The reaction of the lutetium bis(alkyl) complex $Cp'Lu(CH_2SiMe_3)_2(THF)$ (**1**) with 1 equiv of $PhSiH_3$ in hexane at −30 °C gave selectively the mixed alkyl/hydride complex $[Cp'Lu(CH_2SiMe_3)(\mu\text{-}H)(THF)]_2$ (**2**) as colorless crystals in 80% yield (Scheme 1).[9,10] Complex **2** adopts a dimeric structure with two hydride bridges and two terminal alkyl groups.[9] This complex was soluble in toluene, OEt_2, and THF but almost insoluble in hexane. Addition of 1 equiv of $PhSiH_3$ (per Lu) to a C_6D_6 solution of **2** at room temperature generated a new hydride species (**3**) and $PhSiH_2CH_2SiMe_3$, as shown by

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[3] van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J. *Organometallics* **1989**, *8*, 1459.

[4] Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 227.

[5] Hou, Z.; Zhang, Y.; Tardif, O.; Wakatsuki, Y. *J. Am. Chem. Soc.* **2001**, *123*, 9216.

[6] For examples of lanthanide metallocene polyhydride complexes, see: (a) Soloveichik, G. L. *New J. Chem.* **1995**, *19*, 597. (b) Evans, W. J.; Sollberger, M. S.; Khan, S. I.; Bau, R. *J. Am. Chem. Soc.* **1988**, *110*, 439 and references therein.

[7] For intermetallic hydrides, or hydrogen-storing alloys (e.g., $LaNi_5H_x$), see: (a) Guidotti, R. A.; Atkinson, G. B.; Wong, M. M. *J. Less-Common Met.* **1977**, *52*, 12. (b) Percheron-Guégan, A.; Lartigue, C.; Achard, J. C. *J. Less-Common Met.* **1980**, *74*, 1.

[8] For a review on hydride-free organolanthanide clusters, see: Anwander, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 599.

[9] See the Supporting Information for experimental details, including synthesis and spectral and X-ray data of the new compounds **1**−**4**.

[10] For examples of formation of lanthanide hydrides via reaction of lanthanide alkyl complexes with $PhSiH_3$, see: (a) Voskoboynikov, A. Z.; Parshina, I. N.; Shestakova, A. K.; Butin, K. P.; Beletskaya, I. P.; Kuz'mina, L. G.; Howard, J. A. K. *Organometallics* **1997**, *16*, 4041. (b) Arndt, S.; Voth, P.; Spaniol, T. P.; Okuda, J. *Organometallics* **2000**, *19*, 4690. (c) Castillo, I.; Tilley, T. D. *Organometallics* **2001**, *20*, 5598. See also ref 5.

the ^{1}H NMR spectrum (Scheme 1). Although a complete separation of the dihydrido species **3** (hexane soluble) from the oily byproduct $PhSiH_2CH_2SiMe_3$ was difficult, **3** could be isolated as colorless crystals in 38% yield by recrystallization from hexane. A crystallographic study revealed that **3** possesses a tetrameric structure, in which the four Lu atoms form a tetrahedron (Figure 1).[9] There are, in all, eight hydrido ligands in the whole molecule, one being body-centered in a μ_4-H−Lu_4 fashion, two being face-capped in a μ_3-H−Lu_3 form, and five being edge-bridged in a μ_2-H−Lu_2 style. Each Lu atom is thus bonded to one Cp′ and five hydride ligands. The whole molecule is highly symmetric, which possesses two crystallographic mirror planes perpendicular to each other (arbitrarily referred below as plane A and plane B, respectively, for the convenience of explanation). The Lu1 and Lu1* atoms are in one plane (plane A), while the Lu2 and Lu2* atoms are in the other (plane B). The body-centered (H4) and edge-bridged (H3) hydride ligands are located at the juncture of the two planes, while the face-capped hydride ligands H1 and H1* are only in plane B. The four edge-bridged hydrides (H2, H2*, H2**, and H2***) are out of the mirror planes. The Cp′ groups on Lu1 and Lu1* are bisected by plane A, in which the $SiMe_3$ groups (Si2, C15, Si2*, and C15*) are also located. Similarly, the Cp′ groups on Lu2 and Lu2* are bisected by plane B, but their $SiMe_3$ groups are out of this plane and thus result in disorder of the Cp′ ligands. Although this disorder problem did not prevent establishing the connectivity of the whole molecule, further refinement of the structure was difficult.

To make a molecule of lower symmetry, recrystallization of **3** from THF was carried out, which successfully afforded single crystals of **4** suitable for X-ray analysis. Alternatively, hydrogenolysis of **2** in THF also gave **4** in 85% isolated yields (Scheme 1).[11] Complex **4** adopts a tetrahedral structure similar to that of **3**, but one of its four Lu atoms is coordinated to a THF ligand and thus loses the symmetry observed in **3** (Figure 2).[9] The overall structure of **4** is almost the same as that of **3**, except that one of the μ_3-H−Lu_3 bonds in **3** is replaced by a Lu−O(THF) bond in **4** (cf. Figures 1b and 2b). The Lu−H bond distances in **4** range from 1.85(3) Å (Lu4−H4) to 2.49(5) Å (Lu2−H6), which are comparable with those found in **2** (2.06(5), 2.12(5) Å), $[Me_2Si(C_5Me_4)(N^tBu)Lu(\mu\text{-}H)(PMe_3)]_2$ (1.93(6), 2.10(6) Å),[10b] and $[Et_2Si(C_5Me_4)(C_5H_5)Lu(\mu\text{-}H)]_2$ (2.13(4), 2.16(4) Å)[12] and the Yb−H bonds in $[Me_2Si(C_5Me_4)(NCMe_2Et)Yb(\mu\text{-}H)(THF)]_2$ (2.13(9)−2.57(5) Å).[10b] The Lu−Cp′ bond distances in **4** (average 2.568(6)−2.591(5) Å) are normal for lutetium−cyclopentadienyl bonds.

Complexes **3** and **4** are soluble and thermally stable in common organic solvents such as hexane, toluene, and THF. Recrystallization of the THF-coordinated complex **4** in hexane regenerated quantitatively the unsolvated complex **3**. No decomposition or ligand redistribution was observed in THF-d_8 or toluene-d_8, as monitored by ^{1}H NMR. These properties could bode well for further exploration of the chemistry of this new class of hydride species.[13,14]

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Supporting Information Available: Text giving experimental details, figures giving ORTEP drawings, and tables of crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) The reaction of **2** with H_2 in THF seemed to be cleaner and faster than that in toluene. Similar reaction of **1** with H_2 in THF also gave **4**, but this reaction was much slower, which took 2 days for completion. However, the reaction of the yttrium analogue $(C_5Me_4SiMe_3)Y(CH_2SiMe_3)_2(THF)$ with H_2 occurred rapidly to give $[(C_5Me_4SiMe_3)Y(\mu\text{-}H)_2]_4(THF)_n$.[14]

(12) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

(13) Lanthanide metallocene hydride complexes are usually unstable and easily decompose in THF or toluene. For example, see: Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, *10*, 134 and references therein.

(14) Structurally characterizable polyhydrido yttrium complexes could also be isolated in a similar manner.[11] Crystallographic data for $[(C_5Me_4SiMe_3)Y(\mu\text{-}H)_2]_4(THF)$: triclinic, space group $P\bar{1}$ (No. 2), a = 13.016(3) Å, b = 13.153(3) Å, c = 19.699(4) Å, α = 80.521(3)°, β = 86.775(3)°, γ = 74.294(3)°, V = 3202.3(11) Å^3, Z = 2, D_c = 1.254 g cm^{-3}, R (R_w) = 0.0436 (0.0513). For $[(C_5Me_4SiMe_3)Y(\mu\text{-}H)_2]_4(THF)_2$: triclinic, space group $P\bar{1}$ (No. 2), a = 12.435(2) Å, b = 13.533(2) Å, c = 22.017(4) Å, α = 98.938(3)°, β = 92.851(3)°, γ = 114.406(2)°, V = 3306.3(10) Å^3, Z = 2, D_c = 1.287 g cm^{-3}, R (R_w) = 0.0486 (0.0596). Preliminary studies demonstrated that such polyhydrido cluster complexes could show unprecedented reactivities toward various unsaturated organic substrates. Further studies are in progress and will be reported in due course.